Graft copolymerization of hydroxylic methacrylates and ethyl acrylate onto amylopectin*

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(Received 30 May 1991)

In order to achieve new biocompatible materials, graft copolymerization of mixtures of hydroxyethyl methacrylate/ethyl acrylate (HEMA/EA) and hydroxypropyl methacrylate/ethyl acrylate (HPMA/EA) onto amylopectin by ceric ammonium nitrate initiation was carried out. The influence of feed composition was studied with respect to the characteristic grafting reaction yields. Homopolymer formation decreases as the per cent of HEMA monomer increases in the feed and increases as the per cent of HPMA monomer increases in the feed. The values obtained for the percentage grafting were quite high for all the feed compositions.

(Keywords: graft copolymers; starch; amylopectin; biocompatible materials)

Introduction

A hydrogel is defined as a polymeric material which is able to swell in water and retain a significant fraction (e.g. >20%) of water within its structure but which does not dissolve in water[1]. One of the more studied monomers is 2-hydroxyethyl methacrylate (HEMA). Hydrophilicity is an important factor in hydrogels for medical use. In order to achieve a determined hydrophilicity, it is of interest to synthesize hydrogels from hydrophilic monomers in combination with hydrophobic monomers. To this end, one of the more studied copolymers is methyl methacrylate (MMA)/HEMA[2]. Other hydrophobic comonomers have also been used, such as ethyl methacrylate (EMA) and methoxyethyl methacrylate[3].

Recently, composite materials, consisting of collagen and synthetic polymers, have been substituted for pure synthetic polymers to improve tissue tolerance. One of the methods used for the preparation of this new type of hydrogel is graft copolymerization[4]. Among these new copolymers, graft copolymers onto collagen are the most widely studied. The monomers used for grafting were HEMA[4] and HEMA/MMA[5].

With respect to graft copolymers onto polysaccharides, those obtained with HEMA by ^{60}Co irradiation onto cellulose acetate are used for the fabrication of dialysis membranes[6]. However, amylopectin is a carbohydrate with a structure very similar to that of glycogen. And, apart from the biocompatibility of methacrylates which has been largely proved[7], obtaining compounds from the copolymerization of amylopectin with hydrophobic and hydrophilic acrylate mixtures could be of great interest.

Experimental

Materials. The amylopectin used was the commercial product amylopectin UG (Avebe, Holland). The methacrylates were supplied by Merck and were purified as described in the literature[8]. Ethyl acrylate (EA) was supplied by Merck and was purified by washing and distillation under suitable conditions. All the other products were reagent grade or the equivalent.

Method. The mixtures of hydrophilic and hydrophobic monomers grafted were HEMA/EA and hydroxypropyl methacrylate (HPMA)/EA.

The grafting procedure initiated by ceric ammonium nitrate has been given elsewhere[9]. The monomers were mixed before addition. The Soxhlet extraction of the ungrafted acrylic polymer (called homopolymer in this paper) was carried out using ethanol and tetrahydrofuran.

Results and discussion

In order to characterize the reactions the grafting yields described in a previous publication were used[10]. In this way the data shown in *Tables 1* and *2* were obtained.

Grafting of HEMA/EA. As can be seen in *Figure 1*, the percentage grafting efficiency (%GE) remains practically constant for all the composition feeds used, with the exception of pure EA. On the other hand, in the case of pure EA the amount of solid obtained was the highest. As the %GE indicates the amount of homopolymer formed with respect to the amount of graft copolymer, it can be deduced either that HEMA reduces EA homopolymerization or that it favours the introduction of EA into the graft copolymer. In order to

Table 1 Grafting yields for the copolymerization of HEMA/EA onto amylopectin

HEMA/EA (%)	Solid (g)	%GE	%G	%Pol.g.	%CT
100/0	4.31	86.1	129	39.2	50.4
80/20	4.27	88.5	119	38.3	47.4
60/40	4.16	84.1	100	34.6	47.7
50/50	3.75	88.7	93.5	32.7	40.7
40/60	3.48	88.2	83.0	28.4	36.7
20/80	3.64	85.1	67.0	25.9	37.5
10/90	3.20	82.5	68.3	22.8	34.8
0/100	4.99	67.4	79.5	32.2	67.4

*Dedicated by the co-authors to G. M. Guzmán on his nomination as Emeritus Professor of the Basque Country University for his valuable scientific work

0032-3861/92/132860-03

Table 2 Grafting yields for the copolymerization of HPMA/EA onto amylopectin

HPMA/EA (%)	Solid (g)	%GE	%G	%Pol.g.	%CT
100/0	8.03	53.8	129	36.5	90.7
80/20	7.22	51.4	108	30.1	86.6
60/40	5.67	52.9	92.3	23.1	72.8
50/50	5.66	53.6	84.4	22.8	69.4
40/60	5.39	55.3	71.1	22.4	66.0
20/80	4.86	61.8	66.8	23.9	61.2
10/90	4.68	65.8	61.2	23.8	57.9
0/100	4.99	67.4	79.5	32.2	67.4

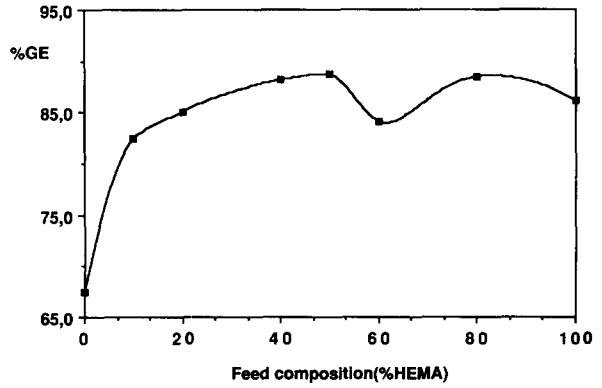

Figure 1 Percentage grafting efficiency (%GE) obtained in the graft copolymerization of HEMA/EA onto amylopectin

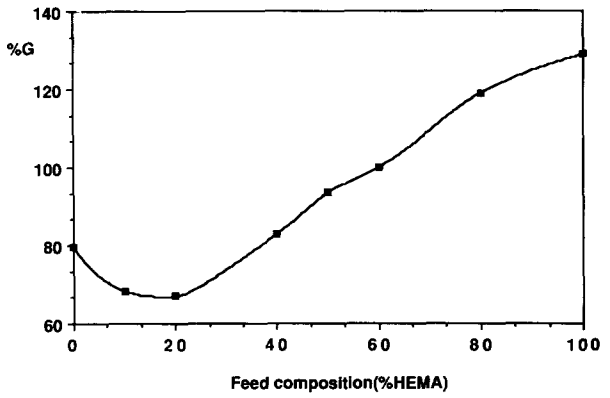

Figure 2 Percentage grafting (%G) obtained in the graft copolymerization of HEMA/EA onto amylopectin

know which of these two premises is true, observation of the other characteristic parameters of the grafting reactions is necessary.

When the amount of HEMA is less than that of EA, the percentage grafting (%G) first decreases and then increases as the HEMA content rises, as shown in *Figure 2*. *Figure 3* corroborates these results. It can be seen that both the percentage of grafted polymer (%Pol.g.) and the percentage total conversion (%CT) have parallel trajectories, from a feed composition of HEMA/EA = 10/90 to 100/0. However, when only the EA monomer is in the feed, the percentage of EA which copolymerizes is lower than that which homopolymerizes. This could mean that small amounts of HEMA decrease the EA reactivity, and when the amount of hydroxylic monomer increases, the percentage of EA in the grafted product decreases, thus decreasing homopolymer formation.

Grafting of HPMA/EA. By comparing *Tables 1* and *2* it can be seen that when HPMA was used the total amount of solid obtained was much higher than when HEMA was used.

In *Figures 4* and *5*, it can be seen that the %GE and the %G are in direct contrast. This means that as the amount of HPMA in the feed increases, both the amount of graft copolymer and the amount of homopolymer increase. So, in the grafting of the mixture HPMA/EA, HPMA favours the polymerization of the acrylate. That means that the HPMA reactivity is higher than that of EA, whereas their reactivities with respect to amylopectin are the same (%Pol.g. ~ constant). On the other hand,

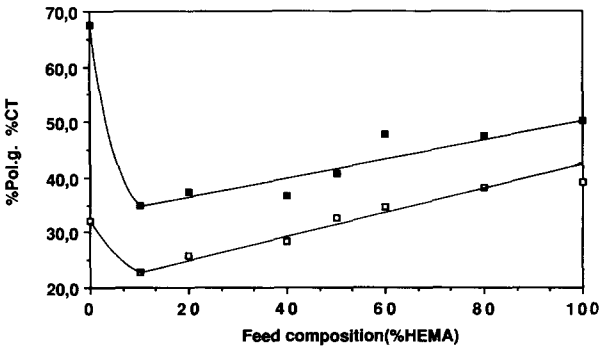

Figure 3 Percentage grafted polymer (% Pol.g., □) and percentage total conversion (% CT, ■) obtained in the graft copolymerization of HEMA/EA onto amylopectin

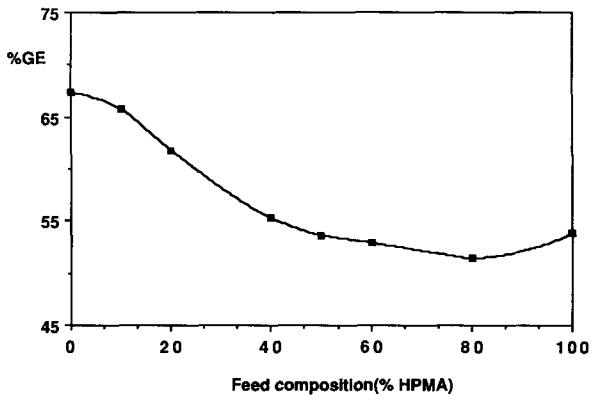

Figure 4 Percentage grafting efficiency (% GE) obtained in the graft copolymerization of HPMA/EA onto amylopectin

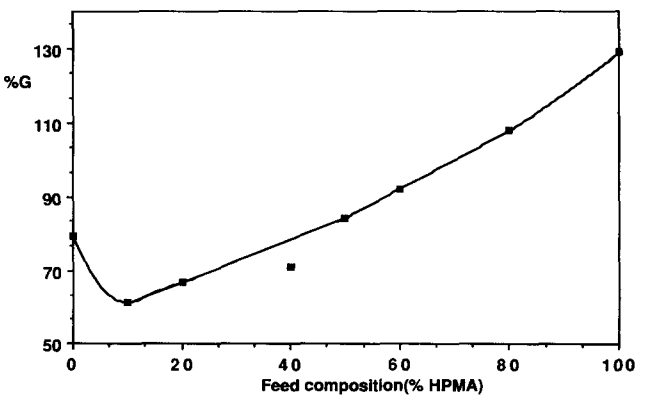

Figure 5 Percentage grafting (%G) obtained in the graft copolymerization of HPMA/EA onto amylopectin

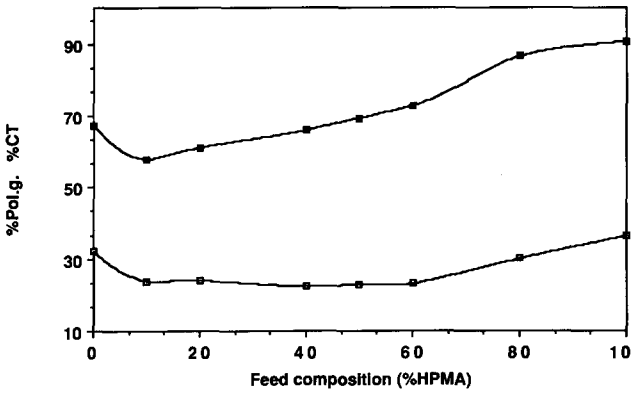

Figure 6 Percentage grafted polymer (% Pol.g., □) and percentage total conversion (% CT, ■) obtained in the graft copolymerization of HPMA/EA onto amylopectin

it can be seen from *Figures 5* and *6* that the yields obtained when pure EA was grafted are different [with this feed composition (EA = 100%) there is a minimum]. However, with a feed composition of HPMA/EA = 40/60 the yields obtained for pure EA are surpassed.

Acknowledgement

CICYT (MAT 90-0912).

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